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THE SOLID-PHASE DECOMPOSITION OF
POTASSIUM AND SODIUM CHLORATES AND
PERCHLORATES IN THE PRESENCE OF
MANGANESE DIOXIDE

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Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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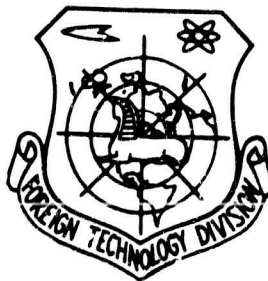
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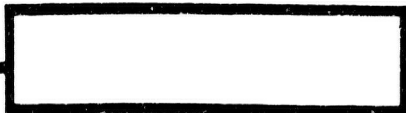
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THE SOLID-PHASE DECOMPOSITION OF POTASSIUM AND SODIUM CHLORATES AND PERCHLORATES IN THE PRESENCE OF MANGANESE DIOXIDE

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The solid-phase decomposition of KClO_3 and KClO_4 in the presence of oxide catalysts has been studied in [1-3]; however, the tests were run at comparatively high temperatures, as a result of which the picture was complicated by the phenomenon of noncatalytic dissociation or the presence of the liquid phase. Both of these hindered subsequent kinetic analysis of the experimental data and their unambiguous interpretation.

In this report we give the results of a study of the catalytic decomposition of potassium and sodium chlorates and perchlorates at low temperatures, when there is practically no dissociation in the absence of a catalyst. In the tests we used the fraction of salt crystals 0.14-0.20 mm in diameter mixed with MnO_2 (~1%). The degree of decomposition of the weighed sample (~300 mg) was recorded using an ADV-200 balance.

The experimental data are satisfactorily described by the topo-kinetic equation $\alpha = 1 - \exp(-kt^n)$, where α is the percentage of decomposed substance; t is the time; n and k are constants [4-6]. In the majority of cases this equation encompasses the entire kinetic

curve (no break in the anamorphosis), and only in one experiment with KClO_3 did parameter n have the value of 1 (in the initial stage) and then 0.5 (in the remaining stage). In the case of NaClO_3 , variation of n as a function of temperature is characteristic (see the table).

Calculated values of kinetic parameter n

Substance	Temperature, °C	α	n
KClO_4	425, 435 445, 465	0.68-0.85	0.66
NaClO_4	350, 370 380	0.7 -0.81	0.63
NaClO_3	240 245 255	0.74 0.85 0.90	0.66 0.72 1.05
KClO_3	315, 320 325, 330 335 335	0.68-0.85 0.20 from 0.30 to 0.90	0.50 1.00 0.50

Judging from the value of n ($0.5 < n < 1$), predominant decomposition of the salts occurs in the diffusion region, and the difference $(1 - n)$ characterizes the measure of immersion of the process into this region [5]. The initial stage of decomposition of KClO_3 at 335°C is an exception; here the general rate of the process is determined by the strictly chemical kinetics at the phase interface. As measurements of the electrical conductivity of a mixture of KClO_3 - MnO_2 showed, this was caused by the temporary appearance of the liquid phase - the eutectic. An analogous phenomenon was detected in experiments with NaClO_3 , where the percentage of the liquid phase decreases with a drop in temperature.

Comparing the volumes of reacting substance and the product, we can estimate the nature of the diffusion resistance of the latter [7]. As follows from such calculations, with decomposition of both chlorates and perchlorates the volume of the forming chlorides is less than that of the initial substances, which predetermines the presence of macropores in the product layer, thus facilitating the feeding and removal of the corresponding components. However, when

KClO₃ decomposes this layer is denser than in the case of KClO₄ and, consequently, here we should expect greater immersion of the process into the diffusion region. The values of n completely agree with this:

$$(1 - n_{\text{KClO}_3}) > (1 - n_{\text{KClO}_4}).$$

The diffusion resistance can be variable (for NaClO₃ as well), and then the kinetic parameter also changes.

CONCLUSION

Comparing the reaction capability of solid substances under conditions of volumetric diffusion [7] and with decomposition of the investigated salts KClO₃ and KClO₄ (two orders higher), in the second case we should assume that an essential role is played by surface diffusion and diffusion along the boundaries of the crystallites.

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